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DESIGN DATA STUDY FOR COATED COLUMBIUM ALLOYS

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A DIVISION OF
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CLEVELAND 17, OHIO

DESIGN DATA STUDY FOR
COATED COLUMBIUM ALLOYS

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ABSTRACT

The work of the first two months of the program has involved principally preparations for the preliminary screening evaluation of seven (7) of the current promising columbium coatings applied to 30 mil Cb-5Zr alloy sheet. Sheet material for the preliminary evaluation phase of the program was obtained, test parameters were established and specimens were prepared and submitted to the various organizations for coating. The preliminary screening tests established will involve the determination of oxidation protective life and bend transition temperatures for each of the seven (7) coating-base metal systems in the as coated, as exposed (2000 and 2600°F) and prestrained (room temperature) + exposed (2000 and 2600°F) condition. Based upon the results obtained from the preliminary evaluation tests, coatings and base alloys will be selected for the design data portion of the program.

Baseline data for the 30 mil Cb-5Zr alloy sheet were experimentally established in this period. Brittle to ductile bend transition temperatures were determined for the uncoated sheet in the as received, stress relieved and heat treated conditions and after exposure in air at 2000 and 2600°F for various short time periods. Surface recession and internal penetration oxidation measurements were also made on the uncoated sheet.

A brief discussion is presented of the design data tests proposed and specialized equipment being constructed.

DESIGN DATA STUDY FOR COATED COLUMBIUM ALLOYS

INTRODUCTION

As refractory metal technology becomes more advanced, the utilization of refractory metal components in operational space and re-entry vehicles becomes a more practical problem. Columbium alloys, because of their high temperature strength and low temperature fabricability, show considerable potential as structural materials. The development of surface alloy coatings for protecting columbium alloys from detrimental oxidation and internal contamination in oxidizing environments has been quite successful on a laboratory scale. However, the practical utilization of any coated columbium alloy depends upon the successful union of coating and base metal to produce a system with useful properties. Until recently, all available data have been generated on coating development programs, and in the absence of standardized evaluation methods almost no comparison could be made of the properties of various coatings and coating-base metal systems. In order to effectively assess the high temperature capabilities of coated columbium alloys for design requirements, truly comparative mechanical property data for coating-base metal systems must be made available to the design engineer.

A program has been initiated by the Bureau of Naval Weapons under Contract NOw-62-0098-c to conduct a comparative evaluation and design data study of presently available protective coatings and columbium base materials. The initial phase of the program will involve a series of screening tests. Coatings supplied by various organizations will be subjected to comparative oxidation tests and bend ductility tests before and after oxidation, under a variety of test conditions. From this screening analysis, the two or three most promising coatings will be selected in conjunction with the project monitor, Bureau of Weapons, for application to one or two columbium base materials for a thorough evaluation of coating-base metal properties.

The design data study will involve tensile testing of coated specimens from room temperature to 2600°F in the as coated condition, after oxidation exposure for various times and temperatures, and after stress-oxidation. Short time stress rupture properties will be determined for temperatures up to 2600°F. Thermal shock tests will be conducted to evaluate the effect of rapid heating and cooling on the protective nature of the coatings. Flaws will be introduced in the coatings to evaluate their ability to self-heal.

Metallographic, microhardness, and electron microscopy techniques will be utilized concurrently with the mechanical testing to further analyse the findings. The program should generate useful mechanical property data for coating-base metal systems, and indicate the influence of various environmental conditions on the protective nature of the coatings and the brittle to ductile transition temperature of the coated substrate.

MATERIALS

Several candidate columbium alloys were considered for the initial screening evaluation tests. However, since these tests are only a preliminary to a more thorough evaluation of the most promising protective coating systems, the alloy selection was based primarily upon availability of a representative alloy in sheet form. Approximately one pound (100 in.^{2}) of 30 mil D-14 (Cb-5Zr) alloy sheet was purchased from DuPont. The ready availability of D-14 sheet permitted fabrication and shipment of the test specimens to the various coating organizations in a minimum amount of time. Table 1 shows the chemical analysis and mechanical properties for this heat of material as reported by the vendor.

Several sets of evaluation specimens were prepared from this sheet, utilizing the following procedure:

1) Specimens sheared to size -

    Oxidation coupons - 0.030" x 0.5" x 0.5"
    Bend Specimens - 0.030" x 0.360" x 1"

2) All edges and corners rounded on a fine abrasive wheel

3) All specimens degreased in trichloroethylene

4) All specimens etched in an aqueous $HF-HNO_3-H_2SO_4$ solution

Each set of evaluation specimens was comprised of 14 oxidation coupons and 14 bend specimens.

COATINGS

The following ten coatings were initially considered for evaluation in this program:

TABLE 1

DU PONT TEST REPORT ON HEAT NO. 14-114 D-14 ALLOY SHEET

Chemical Analysis

PPM O	PPM H	PPM N	PPM C	PPM Ta	Wt. % Zr
207	1	17	29	475	4.8

Mechanical Properties

Test Temperature °F	Tensile Strength PSI x 10^3	Yield Strength PSI x 10^3	Elongation % In./In.	0 T Bend Angle
R.T.-longitudinal	66.1	53.7	24.5	180°
transverse	65.7	53.1	24.5	180°
2200-longitudinal	28.9	16.7	32	
transverse	28.2	16.5	16	

AMF	AMFKOTE
Boeing.	Disil (Columbium)
Chromalloy.	Modified W-2
DuPont.	Fluidized Pack Si-W
G. E.	LB-2 Aluminum Slurry
Pfaudler.	Pack Cementation Silicide (Cr-Mo-Si)
Pratt & Whitney (Canel)	Pack Deposited Silicide (Ti-Cr-Si) or Sn-Al-Cr-Zn Sprayed Slurry
Sylcor.	Hot Dipped Al-Cr-Si Alloy
TRW.	Cr-Ti-Si Vapor Deposited Diffusion Alloy
Vought.	Pack Cementation Silicide (Cr-B-Fe-Si)

Each of the above organizations was contacted by letter and requested to indicate their desire to participate in the screening evaluation tests and to supply cost and delivery information. Boeing, General Electric and DuPont declined to participate, leaving a total of seven coatings from which two or three will be selected based on the evaluation test results for the design data study.

Specimens were shipped during the second week of March to the following organizations: Chromalloy, Pfaudler, Pratt & Whitney (Canel), Sylcor and Vought. American Machine and Foundry agreed to participate in the program, however, shipment of the specimens was deferred awaiting a firm quotation on price and delivery. According to quoted deliveries, the screening tests should commence by the first week of April.

PRELIMINARY SCREENING TESTS

Five relatively simple screening tests have been designed to comparatively evaluate the candidate coatings on 30 mil Cb-5Zr alloy sheet. These tests will involve the following:

1. Metallographic examination of as coated sheet to determine coating microstructure, coating thickness, diffusion zone thickness and thickness of unaffected base metal.

2. Cyclic oxidation exposure in air at 2600, 2300, 2000 and 1600°F for 150 hours or to failure, whichever occurs first. Metallographic examination of specimens will be made after exposure.

3. Room temperature bend-ductility evaluation of coated sheet. Specimens will be bent at room temperature over a 4T radius under test conditions based on MAB testing specifications.

4. Pre-strain + oxidation tests combining room temperature bend-deflection in the elastic and plastic region with subsequent static oxidation exposure at 2600°F for two hours and 2000°F for ten hours. Bend tests will then be conducted at room temperature.

5. Oxidation exposure for 20 hours at 2600°F and 100 hours at 2000°F followed by room temperature bend test.

The cyclic oxidation tests will be performed in globar heated air furnaces, with specimens representing each individual coating simultaneously exposed at each of the oxidation temperatures. Cyclic oxidation will involve cooling the specimens to room temperature for observation once each hour for 8 hours, followed by 16 hours of static exposure for each 24 hour period. Three duplicate specimens will be tested for each condition. Metallographic analysis and microhardness measurements will be utilized after oxidation to determine the permeability of the coatings to oxygen and/or nitrogen.

Bend testing will be conducted under the specifications recommended by the Refractory Metal Sheet Rolling Panel of the Materials Advisory Board. For 30 mil sheet this will involve the following parameters:

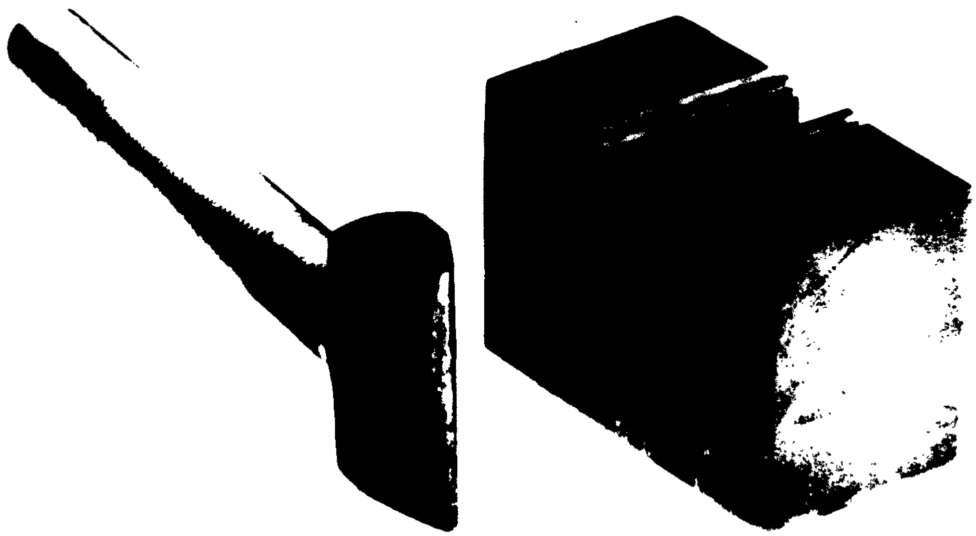
1) Specimen width - 12T - 0.360"
2) Bend radius - 4T - 0.120"
3) Beam support distance - 15T - 0.450"
4) Cross head speed - 10 inches/minute

Figure 1 is a photograph of the Instron tensile machine equipped with the elevated temperature bend test apparatus. Figure 2 is a photograph of the bend fixture.

The room temperature bend ductility tests on as coated sheet specimens will indicate the effect of the coating and coating processes on the low temperature ductility of the coated substrate. Excessive oxygen or nitrogen or hydrogen, used as a carrier gas in the coating process, could increase the base metal ductile to brittle transition temperature above the normal handling temperature.

INSTRON TENSILE MACHINE EQUIPPED WITH ELEVATED TEMPERATURE BEND TEST APPARATUS

FIGURE 1



BEND TEST FIXTURE

FIGURE 2

With a relative baseline ductility established for the as coated condition, coated specimens will then be exposed in an oxidizing atmosphere for 20 hours at 2600°F and 100 hours at 2000°F, and subsequently bend tested at room temperature. Coatings which are poor barriers to the diffusion of oxygen could permit severe embrittlement of the coated substrate prior to any external evidence of coating failure.

Baseline data for the Cb-5Zr alloy sheet (30 mil) was established for the screening tests by bend testing uncoated D-14 alloy sheet in the stress relieved condition (1 hour at 1800°F in vacuum), after 10 hours vacuum heat treatment at 2600°F, and after short time exposure in air at 2000 and 2600°F. The bend tests were conducted over the temperature range -320 to 1200°F. Figure 3 shows a plot of the permanent bend angle as a function of test temperature for each of these conditions. This data is also listed in Table 2.

The D-14 alloy was ductile at -320°F both in the stress relieved condition (1 hour at 1800°F) and after 10 hours vacuum heat treatment at 2600°F. Figure 4 shows photomicrographs illustrating the degree of grain growth resulting from the 2600°F heat treatment.

The severity of the extremely short time oxidation exposure on the uncoated columbium alloy at 2000 and 2600°F is evidenced by the rapid increase of the ductile to brittle transition temperature (Figure 3). Oxidation for 0.1 hour at 2000°F raised the transition temperature from below -320°F to approximately -100°F, after 0.3 hour to 1100°F, and after 0.5 hour at 2000°F the 30 mil Cb-5Zr alloy sheet was brittle above 1200°F. Oxidation for 0.1 hour at 2600°F rendered the 30 mil sheet brittle above 1200°F.

Figure 5 shows photomicrographs of the specimens oxidized at 2000°F. The internal penetration of oxygen is observed as the advancing interface of oxygen contaminated substrate across the cross section. Microhardness impressions are shown in the photomicrographs and the hardness values are plotted as a function of distance from the original surface in Figure 6. At 2000°F the D-14 alloy was hardened by oxygen to a depth of 15 mils, completely through the 30 mil sheet, in 0.5 hour. At 2600°F the entire specimen cross section was severely hardened in only 0.1 hour of oxidation.

Figure 7 is a plot of internal oxygen contamination and cross sectional surface recession as a function of time at 2000 and 2600°F.

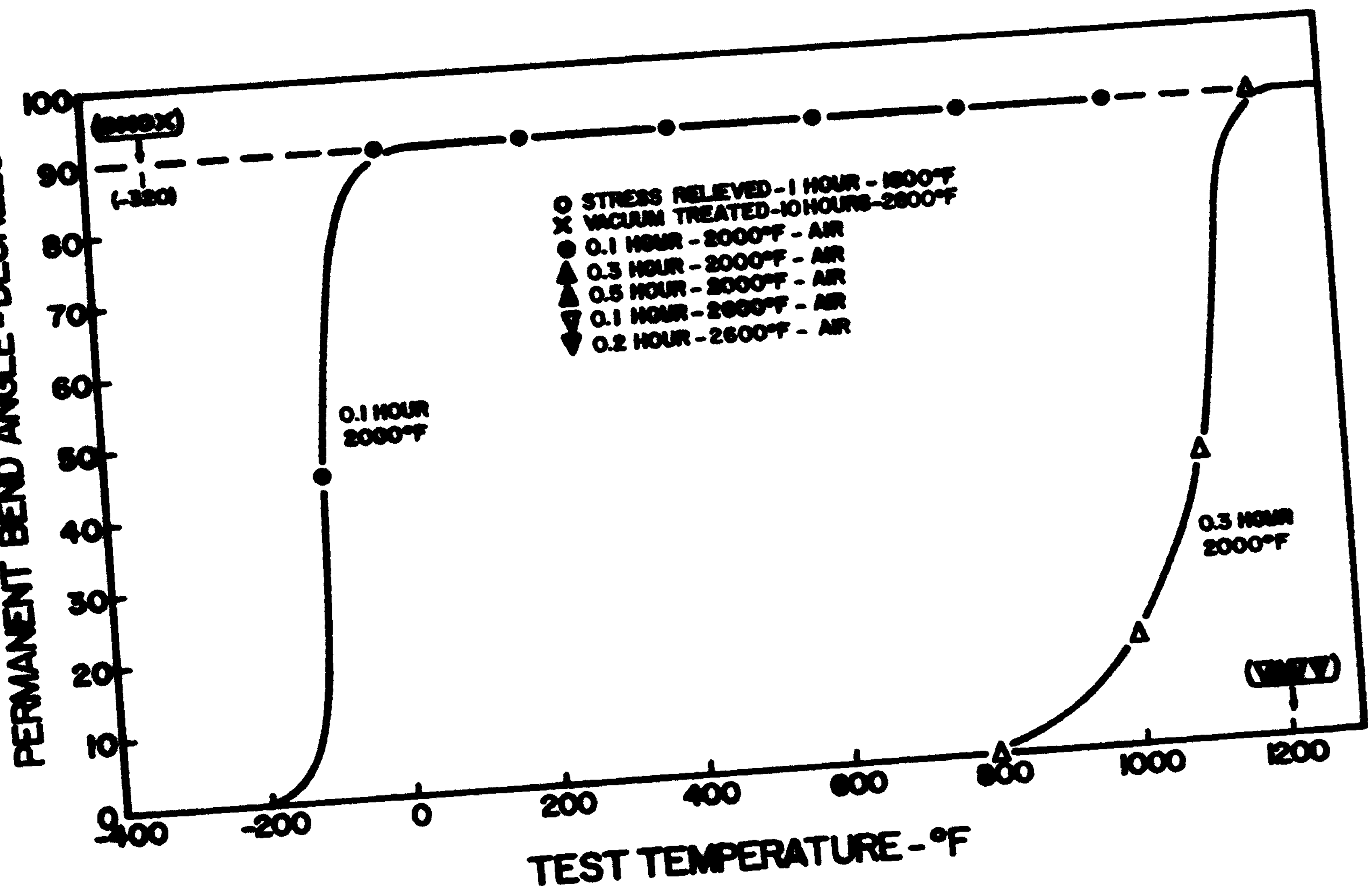


FIGURE 3 BEND TEST DATA FOR VACUUM HEAT TREATED AND AIR OXIDIZED 30 MIL D-14 ALLOY SHEET

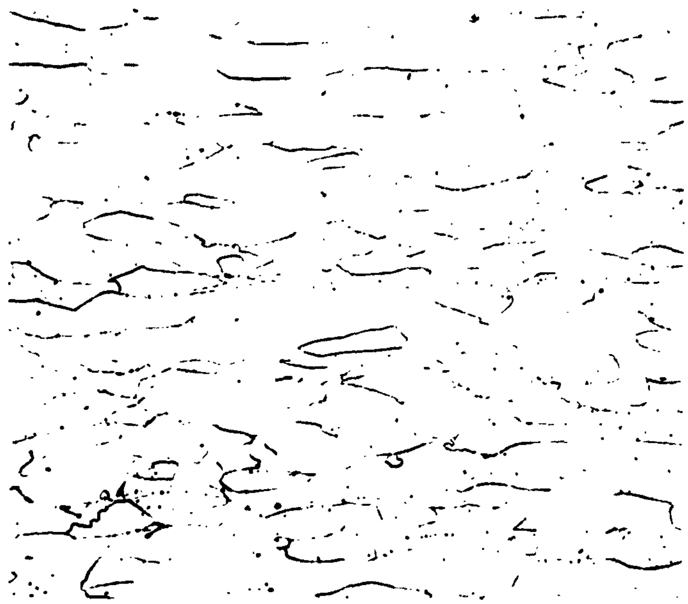
TABLE 2

BEND DUCTILITY TESTS ON D-14 ALLOY SHEET AT VARIOUS TEMPERATURES (1)

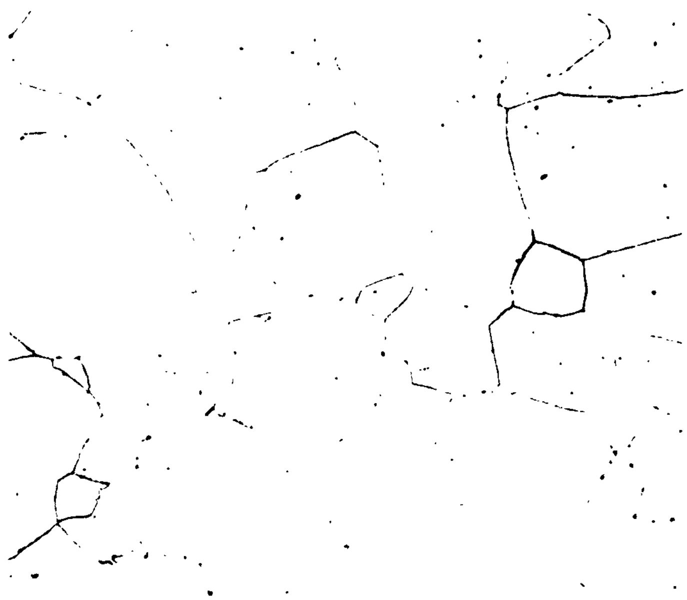
Degrees Bend (4 T Radius)

Specimen Condition	Bend Test Temperature - °F									
	-320	-90	R.T.	200	400	600	800	1000	1100	1200
Stress Relieved	90, 90									
Vacuum Treated-										
10 Hours-2600°F	90, 90									
Oxidized-										
0.1 Hour-2000°F		45	90	90	90	90	90	90		
0.3 Hour-2000°F								15	40	90
0.5 Hour-2000°F							0	0		0, 0
0.1 Hour-2600°F										0, 0
0.2 Hour-2600°F										0, 0

(1) Sheet Thickness - 30 Mils
Tests Conducted According to MAB Specifications



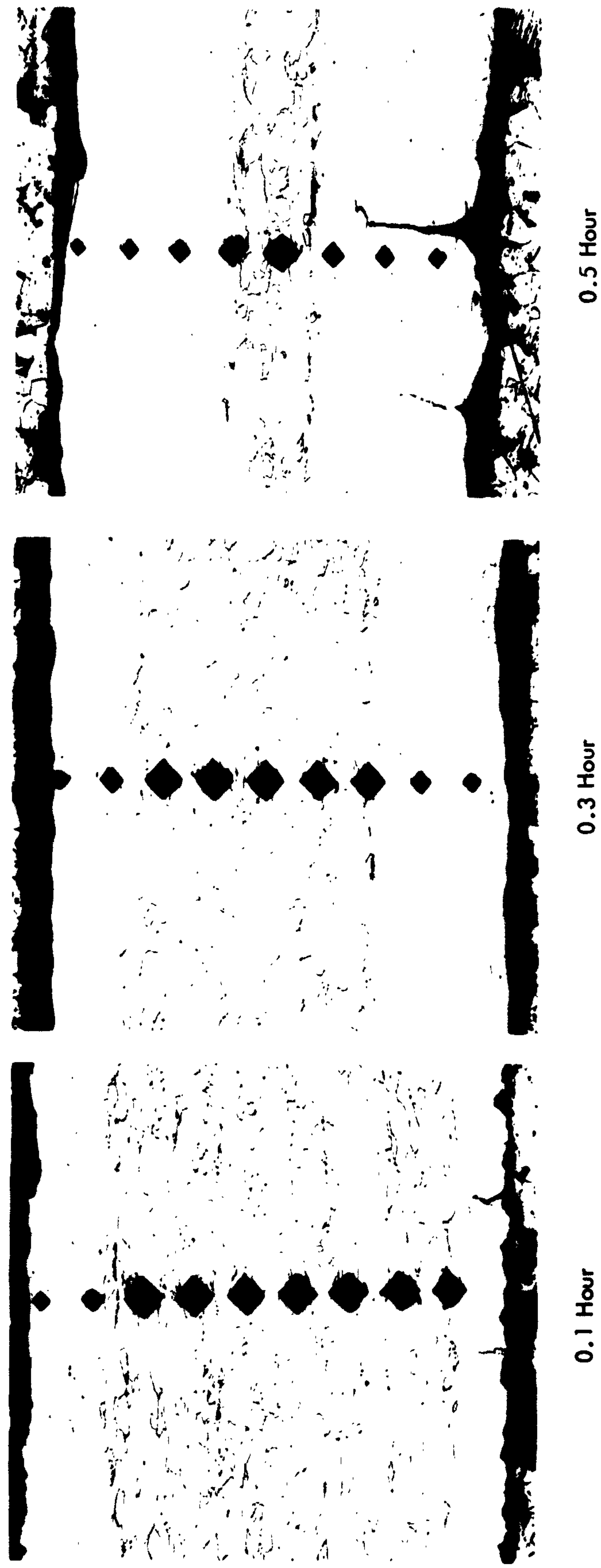
1 Hour - 1800°F



10 Hours - 2600°F

PHOTOMICROGRAPHS SHOWING D-14 ALLOY SHEET STRUCTURE AS STRESS RELIEVED (1 HOUR-1800°F) AND AFTER VACUUM HEAT TREATMENT FOR 10 HOURS AT 2600°F 250 X

FIGURE 4



PHOTOMICROGRAPHS SHOWING OXYGEN PENETRATION IN
D-14 ALLOY OXIDIZED IN AIR AT 2000°F 100 X

FIGURE 5

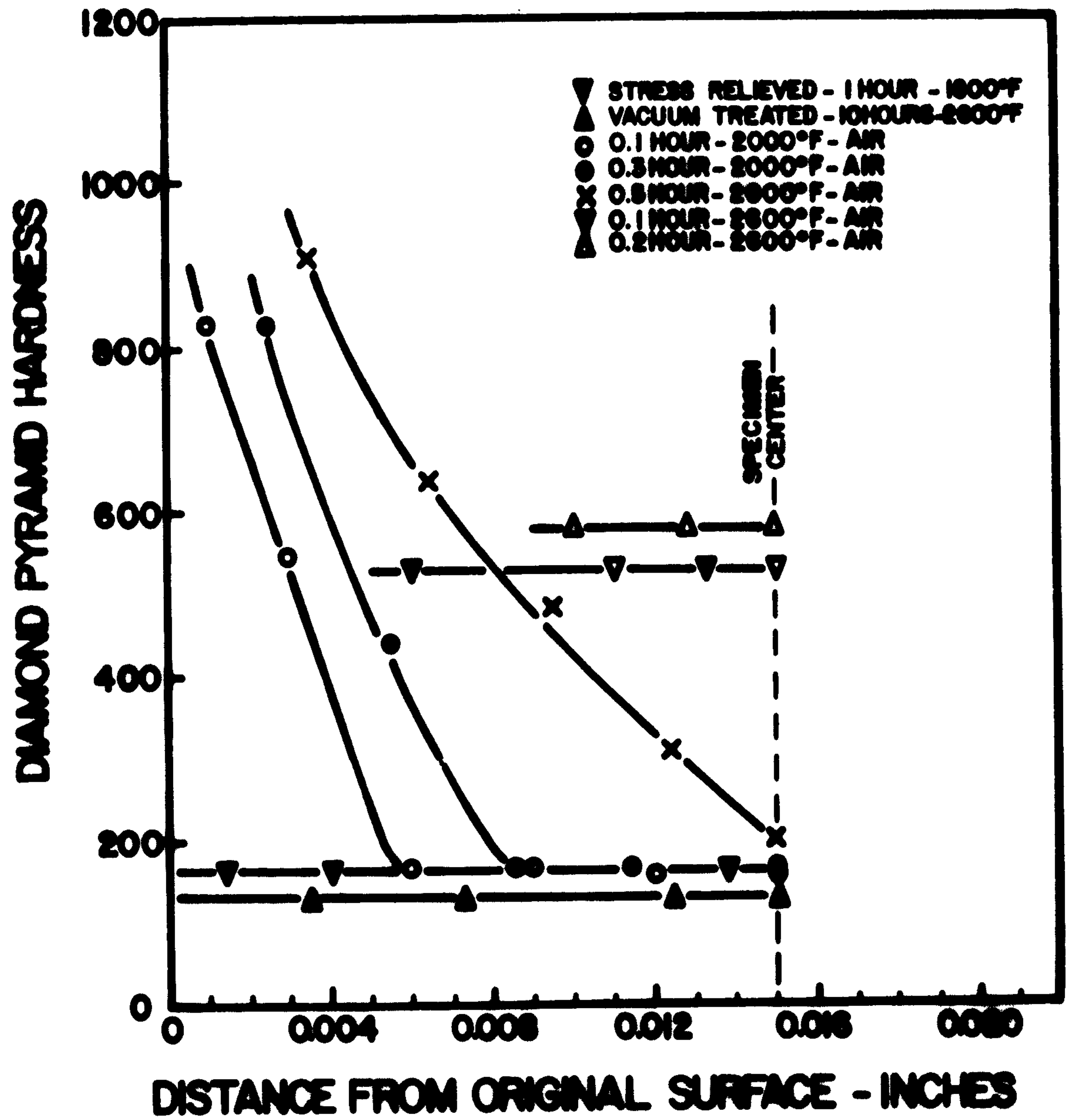


FIGURE 6 MICROHARDNESS TRAVERSES ACROSS 30 MIL D-14 ALLOY SHEET FOR HEAT TREATED AND OXIDIZED CONDITIONS

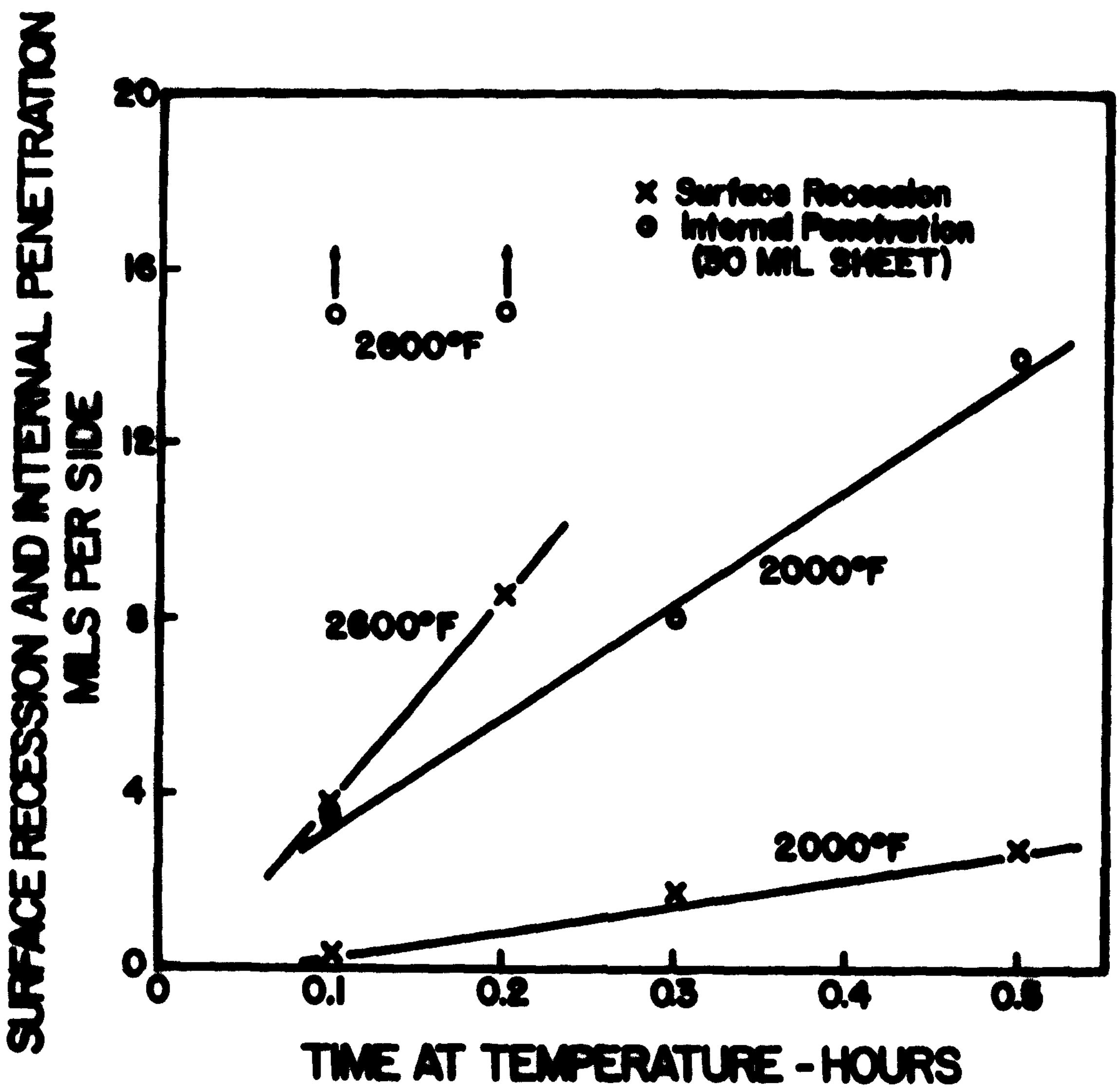


FIGURE 7 SURFACE RECESSION AND INTERNAL PENETRATION FOR OXIDIZED D-14 ALLOY AS A FUNCTION OF TIME AT 2000 AND 2600°F

This data is also listed in Table 3. Internal penetration was taken as the depth of the metallographically observed interface which was produced on polishing by the differential hardness. This interface is not quite coincident with the depth of contamination indicated by the microhardness traverses. Surface recession, resulting from conversion of the base metal to an oxide scale, increased by a factor of approximately 10 from 2000 to 2600°F.

A comparison can now be made of the bend transition temperature with the photomicrographs, microhardness traverses, and measurements of oxygen affected metal. Oxidation of the unprotected 30 mil D-14 alloy sheet for 0.1 hour at 2000°F contaminated approximately 25% of the original cross section, raising the transition temperature from below -320 to -100°F. In 0.3 hour at 2000°F 75% of the cross section was affected by oxygen and the transition temperature was increased to 1100°F. Oxygen completely penetrated the 30 mil sheet in 0.5 hour at 2000°F and 0.1 hour at 2600°F, embrittling the metal as measured in the bend test to above 1200°F.

Load-deflection standards were also established for prestraining coated bend specimens prior to oxidation testing. Figure 8 is a plot of the applied load as a function of beam deflection for stress relieved and recrystallized Cb-5Zr alloy sheet prestrained in the bend test apparatus. From this graph deflections can be selected for prestraining coated specimens in the elastic and plastic deformation regions. Subsequent oxidation for 2 hours at 2600°F and 10 hours at 2000°F will demonstrate the relative room temperature ductility of the various coatings and their ability to self-heal coating flaws imposed by cracking during low temperature prestraining. Bend tests at room temperature will further indicate substrate contamination if external failures are not evident.

PROPOSED DESIGN DATA STUDY

At the conclusion of the screening evaluation tests the results of these tests will be carefully analysed and the two or three most promising coatings selected for the design data study. This second phase of the program will consist of a more intensive evaluation of certain specific coating-base metal systems to determine the following design criteria:

1. Tensile properties (ultimate and yield strengths, elongation and modulus of elasticity) for each coating-base metal system at temperatures from room temperature to 2600°F and up to failure, depending upon the coating system. (R.T., 400, 800, 1200, 1600, 2000, 2300, 2500 and 2600°F).

TABLE 3

OXIDATION DATA FOR D-14 ALLOY OXIDIZED IN AIR AT 2000 AND 2600°F(1)

Oxidation Temperature °F	Time-Hours	Surface Recession Mils Per Side	Internal Penetration (2) Mils Per Side
2000	0.1	0.2	3.5
2000	0.3	1.7	8.0
2000	0.5	2.7	14.0
2600	0.1	3.5	>15.0
2600	0.2	8.5	>15.0

(1) For 30 Mil Sheet

(2) Metallographically Observed

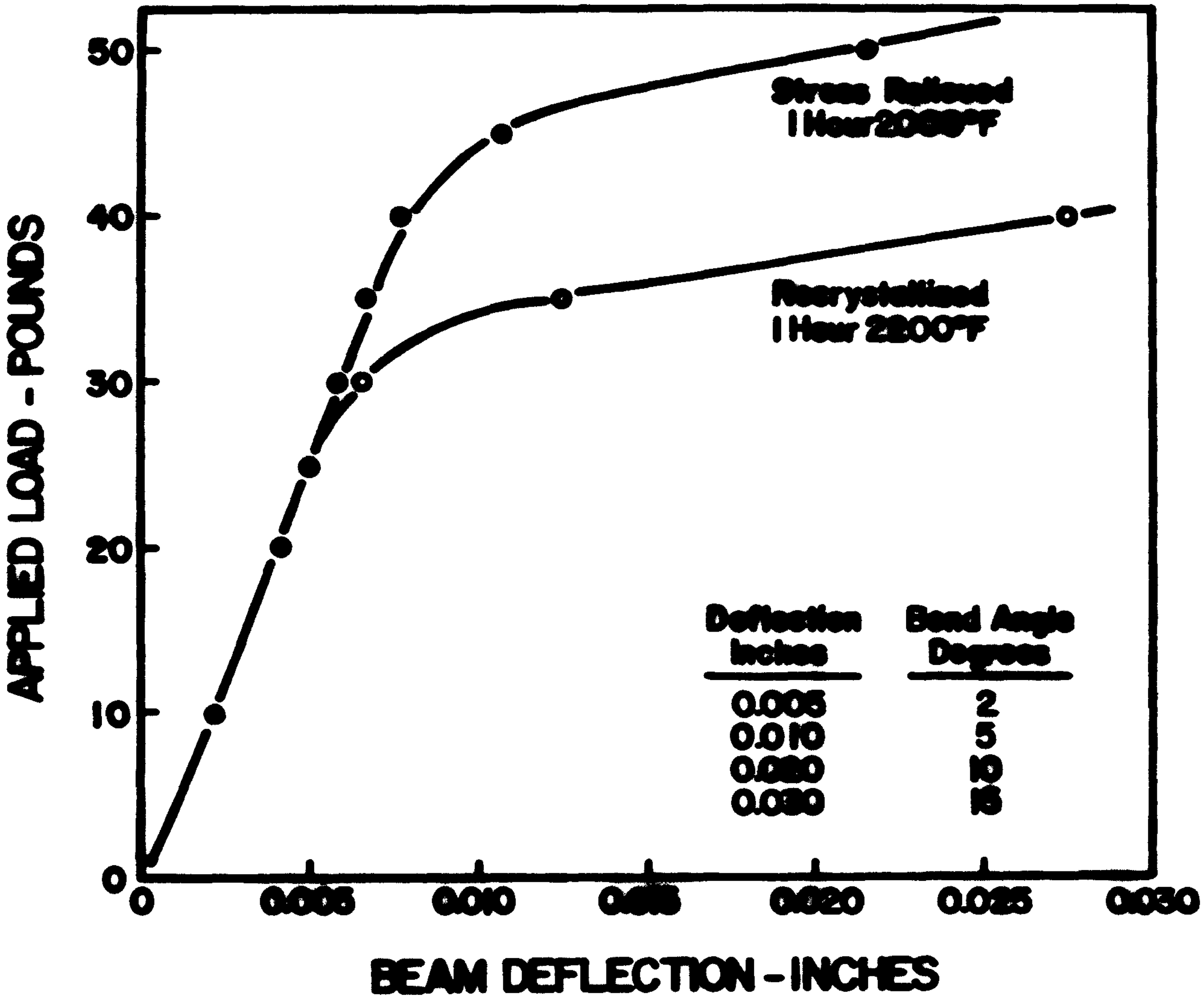


FIGURE 8 BEAM DEFLECTION AS A FUNCTION OF APPLIED LOAD FOR D-14 ALLOY STRESSED IN THE BEND TEST APPARATUS

2. Tensile properties for each coating-base metal system at room temperature after exposure to air for various times at temperatures from 1600 to 2600°F. The tensile properties of the exposed coating-base metal systems will be correlated with those of the unexposed systems to determine the effect of exposure on the transition temperature of the base alloy and to establish the maximum useable temperature range for each system. Since the transition temperature of columbium alloys is very sensitive to small changes in oxygen content, the tensile transition temperature and its influence on low temperature ductility is a very good measure of the protective characteristics of a coating. If a coating prevents internal penetration of oxygen into the base metal then no sharp rise in transition temperature will occur. Test specimens will be sectioned and metallographic studies (both optical and electron microscopic) and hardness measurements will be made for correlation with the mechanical test data.

3. Tensile properties of each coating-base metal system at room temperature, after stress-oxidation at 2000-2600°F. Coated tensile specimens will be loaded at a predetermined percentage of the base metal yield strength of the test temperature, and exposed in air at these temperatures. This will provide an evaluation of the protective nature of the coatings at elevated temperature under a stress sufficient to produce creep of the base metal.

4. Self-healing ability of each coating. Designed flaws will be produced in the coatings prior to exposure by prestraining or stress cracking below the ductile-brittle transition temperature for the coating, drilling a 1/64" diameter hole through the coating into the base metal or by ballistic impacting the coating a low temperature.

5. Thermal shock resistance of each coating-base metal system cycled from 2600 to 250°F (The lower temperature is arbitrary and based only on the cycle time set for the test since the rate of cooling is quite slow below 500°F, and consequently the incident thermal shock is low.). The criterion of failure will again

be the effect of repeated thermal shock cycling on the measured transition temperature of the coated system correlated with metallographic and hardness measurements.

6. Short time stress rupture properties of each of the coating-base metal systems at 1600, 2000, 2300 and 2600°F under identical load and time conditions.

At the completion of the program a comprehensive design data summary of columbium coatings will be prepared covering the properties determined in the experimental phase of the program. In this manner it will be possible to acquire comparative data and to establish useful design criteria for the utilization of several coated columbium systems.

EXPERIMENTAL EQUIPMENT

Two pieces of equipment are being designed and constructed for this evaluation program. The elevated temperature tensile tests will be conducted in an Instron tensile machine, and the tensile specimens will be heated in an infrared radiant heating chamber. Figure 9 is a cross sectional sketch of the proposed furnace. A water cooled cylindrical reflector will be used to reflect the radiant energy from four infrared quartz lamps. Superalloy tensile specimen holders will be housed in refractory shields, and water cooled if necessary, in order to maintain the holder temperature below 2000°F. Quartz lamps provide rapid heating rates to temperatures in excess of 2600°F, and can be confined in a relatively small chamber adaptable to the tensile machine.

The second furnace being constructed is a globar heated multiple rack stress-oxidation furnace, shown in Figure 10. This furnace will have the capacity of stress oxidation or stress rupture testing five specimens simultaneously, and independent of one another, at temperatures up to 2800°F. The tensile specimen holders will be made entirely of refractories, and will be assembled as part of a refractory tube which can be inserted into the furnace hot zone through the base of the furnace. Dead weight, vertical, external loading will be applied through the refractory specimen holder and loading rod. Continuous creep measurements will be made with a dial gage beneath each weight pan. Temperature measurements of each specimen and control of the furnace will be accomplished by platinum-platinum + 10% rhodium thermocouples and checked by optical pyrometry.

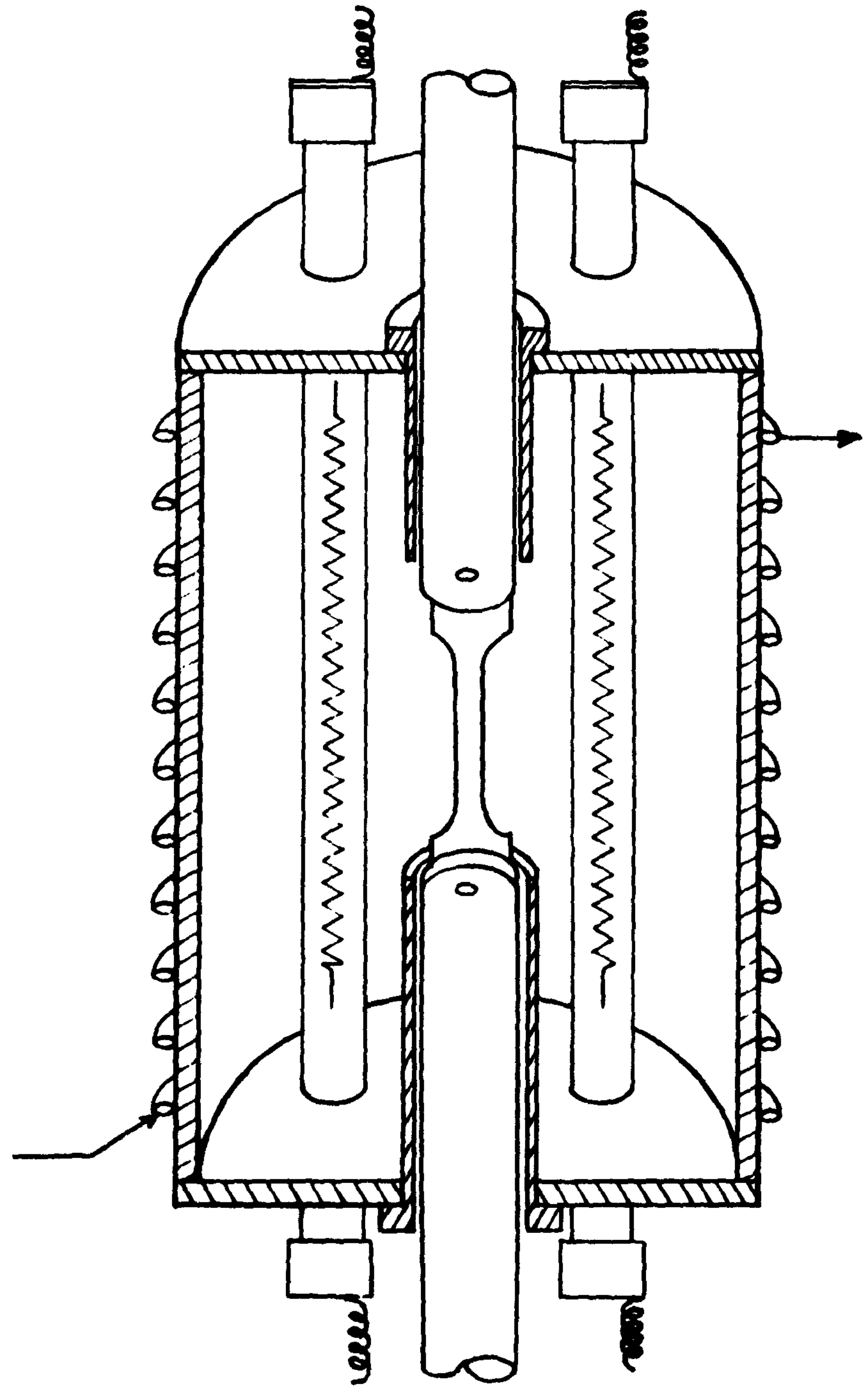


FIGURE 9 CROSS SECTION OF INFRARED RADIANT HEATING FURNACE FOR TENSILE TESTING Approx. 1 X

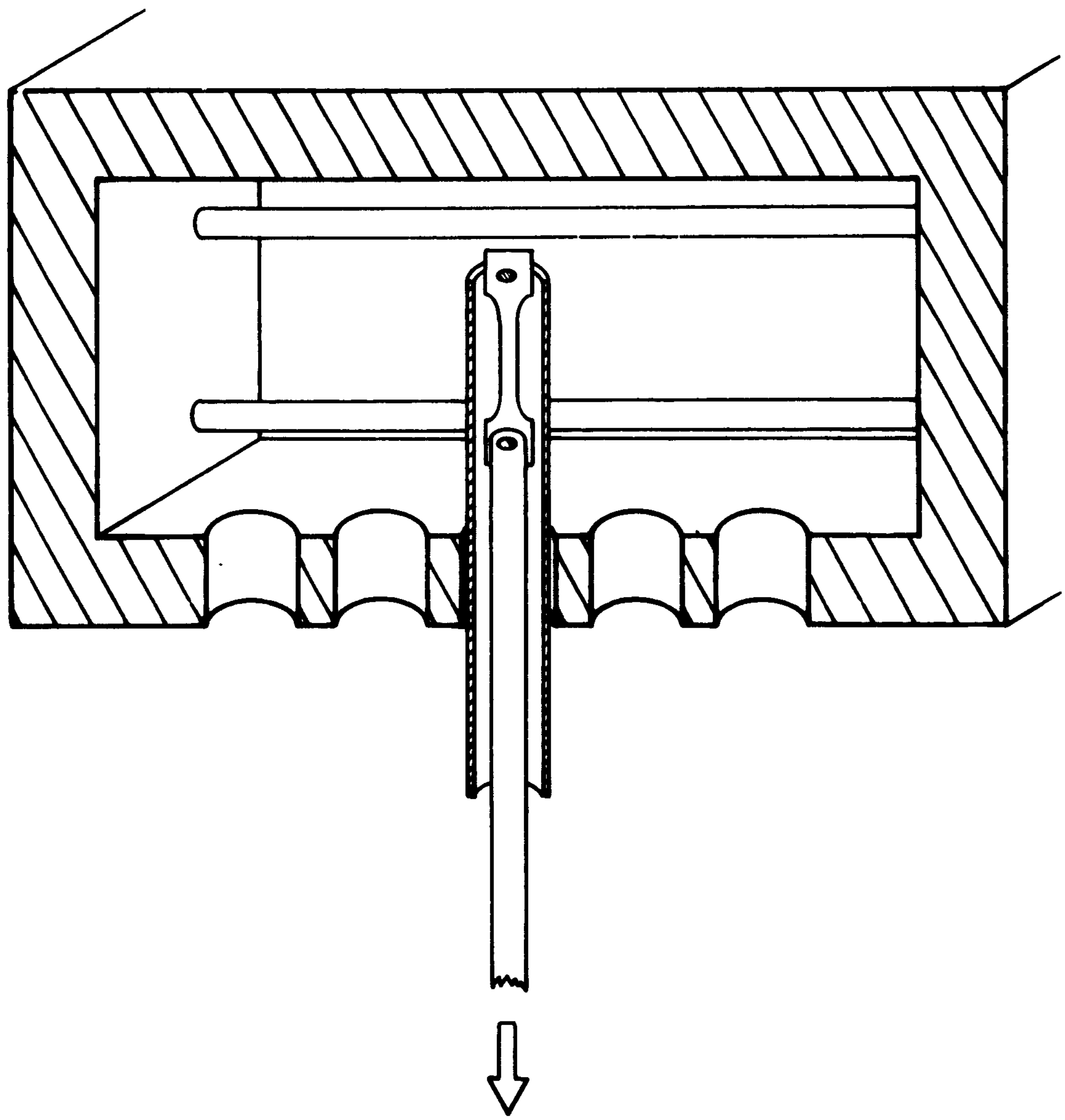


FIGURE 10 CROSS SECTION OF THE HEARTH OF A GLOBAR HEATED MULTIPLE RACK STRESS OXIDATION FURNACE
Approx. 1/3X

This First Bimonthly Report is submitted by Materials Processing Department, Thompson Ramo Wooldridge Inc., in accordance with the provisions of Contract NOw-62-0098-c, Bureau of Weapons, Navy Department.

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